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THE EFFECT OF Al AND Ca IMPURITIES ON THE PROPERTIES OF QUARTZ CERAMICS

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The effect of aluminum and calcium impurities on quartz ceramic properties is studied and its causes are elucidated. A possible mechanism of migration of these impurities from gypsum molds into ceramic crock in the course of casting is considered. The necessity of the presence of Al_2O_3 , if quartz ceramic products are used at temperatures above 1450°C , is stated.

Quartz ceramics are widely used in different areas, in particular, in optical glass production. This material is used to produce crucibles, agitators, and pool beams for furnace tanks operating in contact with glass mixture at a temperature of 1600°C .

Quartz ceramic products are traditionally molded in gypsum molds by the slip casting method. In order to obtain slip, the material (quartz glass) is ground in ball mills in a certain ratio between the material, balls, and water (USSR inventor's certificate 590302). Generally, standard porcelain mills and urolite balls are used. In this case, owing to abrasion of the porcelain and urolite, Al_2O_3 appears in the slip, and its mass content reaches 0.1% and more.

In the context of the high requirements for the purity of glass material used for making glass of special clarity, the balls and the lining of the mills are made of melted quartz in order to prevent contamination of the slip with alumina and other impurities. In this case, the slip contains around 0.02% Al_2O_3 , which is determined by the chemical composition of the initial material.

The practice of using stirring rods made of quartz ceramics in combustion furnaces proved that the method of slip manufacture affects the service behavior of the product. With a temperature in the furnace of 1450°C and more, stirring rods molded from slip prepared in a quartz mill exhibit surface defects, such as oval (scale)-shaped spalling located over the entire surface of the stirring rod. (Fig. 1). The stirring rods made of slip prepared in a porcelain mill do not exhibit this kind of defect.

The difference in the behavior of the articles is probably related to the different content of Al_2O_3 . For example, addi-

tion of more than 0.1% alumina to quartz glass changes the character of glass crystallization, increases its strength, and decreases thermal deformation [1].

In order to investigate the effect of alumina on shrinkage of quartz ceramic in sintering, experiments involving step-wise heating of samples with 0.1, 0.5, and 1.0% additions of Al_2O_3 were carried out. At first the samples were cured for 2 h at a temperature of 1200°C and then rapidly heated to 1300°C and cured for another 2 h. Certain samples were extracted from the furnace after preassigned time spans. The results of the experiments (Fig. 2) indicate the positive effect of Al_2O_3 additives. With an Al_2O_3 content equal to 0.5% and more, shrinkage at 1200°C decreased by nearly half, and the additional shrinkage with a temperature increase is significantly lower in samples with Al_2O_3 additives than in a sample without silica additives.



Fig. 1. Stirring rod after heat treatment in a glassmaking furnace at 1450°C .

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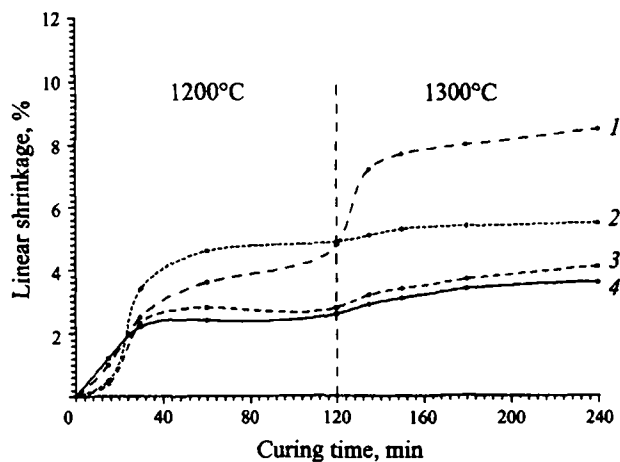


Fig. 2. Kinetic curves of shrinkage of activated samples in stepwise heating: 1) initial SiO_2 ; 2, 3, and 4) samples with addition of 0.1, 0.5, and 1.0% Al_2O_3 , respectively.

It is stated in [2] that slip prepared in a mill with a quartz glass lining and balls of melted quartz has pH from 4.0 to 6.0. On the other hand, the appearance of alumina in slip on milling quartz glass with alundum balls in a mill lined with corundum tiles results in a decrease in pH to 3.0–3.7. The authors of [2] attribute this modification of slip pH to the reaction between silica and alumina sols emerging in milling and formation of aluminosilicic acid which is stronger than silicic acid. This explanation seems probable, since it was demonstrated in [3] that mixed silica and alumina gel behaves (in particular, in interaction with indicators) as a strong polybasic acid (it should be noted that the product used contained 9% Al_2O_3).

Similar results were obtained in our experiments. Three slips were prepared: in a mill with quartz glass lining and quartz glass balls (I) or uralite balls (II), and in a porcelain mill with uralite balls (III). In the first case, the slip had pH of 6.5–6.8, in the second case, pH of 5.8–6.5, and in the third case, pH from 4 to 5. The absolute values differ from the data in [2], but the tendency of the pH to decrease with an increase in the Al_2O_3 concentration in the slip is maintained.

Samples made of the slips specified were tested by the method of x-ray spectrometric microanalysis (XSMA). The intensity of AlK_α radiation was measured with a sharply focused probe in arbitrarily chosen points in the bulk and surface layer ($\sim 30 \mu\text{m}$) of a sample. A leucosaphire single crystal was taken as the reference standard. The background was determined on Ku-1 quartz glass not containing Al_2O_3 . The measurement results are listed in Table 1.

It is seen that the Al content increases in the direction of $\text{I} \rightarrow \text{II} \rightarrow \text{III}$, and the concentration of Al is the same in the surface layer and in the sample body. At the same time, some areas are found in which the concentration of Al exceeded the average value by one order of magnitude.

In order to assess the dimensions of the areas with increased Al content, scanning and recording of the x-ray in-

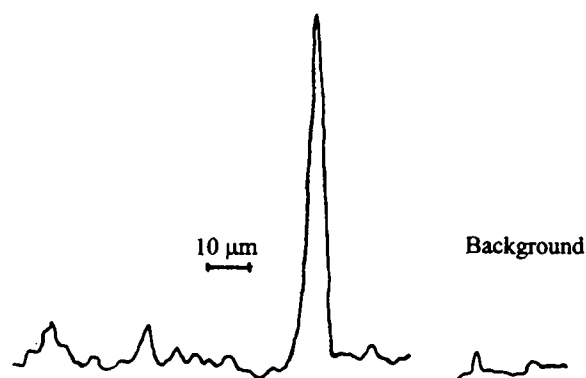


Fig. 3. AlK_α -radiation intensity curve $10 \mu\text{m}$ Background.

tensity curves were used. The bulk and the surface layer of samples II and III were analyzed. Scanning was carried out both parallelly and perpendicularly to the sample surface. A typical curve recorded at a scanning rate of $0.25 \mu\text{m}/\text{sec}$ is represented in Fig. 3.

It is seen from Fig. 3 that the extent of the areas with an increased concentration of Al reaches $10 \mu\text{m}$. The presence of such sites in the samples can be attributed only to breaking off of mill ball and lining material particles in the course of grinding the quartz glass.

On the other hand, the following experiment is evidence of formation of aluminosilicic acid. Through elutriation, a finely disperse (up to $1 \mu\text{m}$) fraction was extracted from slip III, and a sample was formed by electrophoretic precipitation at a constant voltage. After firing the sample at 1200°C , semitransparent glass was obtained, and its analysis by the XSMA method revealed the presence of aluminum in the amount of 0.3%, i.e., twice the average concentration of Al (Table 1).

This is the reason for the assumption that part of the Al_2O_3 migrating into the slip as a result of grinding of mill balls and mill and lining material in combination with silica generates a sol with increased acid characteristics, and the other part of the Al_2O_3 is present in the slip in the form of particles up to $10 \mu\text{m}$ in size.

According to [4], two processes take place in the course of crock formation out of argillaceous slip in a gypsum mold: dehydration of slip due to absorption of water into the mold, and coagulation of slip due to ion exchange between the diluent ions and Ca^{2+} cations of the gypsum mold. The presence of local flocculation with migration of Ca^{2+} cations at the boundary between cast and mold is established as well in [5].

In contrast to argillaceous slips and suspensions of non-plastic oxides, a slip made of quartz glass does not contain deflocculants (diluent). It is a suspension whose sedimentation stability is conditioned by formation of an electric double layer as a result of a chemical reaction between glass and water in the course of mechanical grinding. In this case,

the possibility of exchange between Ca^{2+} cations of the gypsum mold and any ions of slip becomes less probable, since the content of impurities, especially Al and Ca in the slip is insignificant (the concentration of Ca is lower by one order of magnitude than the content of Al indicated in Table 1), and the form of their existence (ions, colloidal particles, etc.) is not known.

In order to elucidate the possibility and mechanism of migration of calcium from the gypsum mold to the product crock, the distribution of calcium in ceramics obtained from slips I and II was analyzed with the XSMA method. The measurements were performed with a sharply focused probe directed from the surface to the center of the sample with a 5 μm step. A calcium fluoride crystal was used as reference standard, and the background was measured on Ku-1 quartz glass with a spectrometer adjusted to the CaK_α line.

It was found that calcium is present only in the surface layer about 10 μm thick and is distributed over that layer non-uniformly: with an average content of 0.26% (sample I) and 0.12 (sample II), some sites up to 10 μm in size were found with a local Ca content of up to 10 and 1.3%, respectively.

Assuming that the sites with a high calcium concentration are gypsum particles broken away from the mold in slip casting, they should contain sulfur as well. However, the firing temperature of quartz ceramics (1200°C) significantly exceeds the temperature of decomposition of gypsum (900°C). This explains the absence of sulfur in the fired ceramics.

Therefore, a polished section of non-fired sample I was investigated. A single crystal of zinc sulfide was used to adjust the spectrometer to the line of sulfur and as reference standard.

The measurements revealed that sulfur was present as well in the areas with an increased calcium concentration, i.e., these sites are gypsum particles broken away from the mold. Therefore, at least some of the calcium appears in the surface layer of ceramics not due to ion exchange, but as a result of mechanical destruction of the gypsum mold. The result obtained agrees well with the known fact of deterioration of the quality of gypsum mold working surfaces and the increase in the mold internal dimensions in the process of service, which limits the service life of these molds.

The presence of calcium in the surface layer of ceramics obtained from "pure" slip (sample I) is undesirable in case of high-temperature operating conditions for the product. Ac-

TABLE 1

Al weight content	Method of analysis	Type of slip			
		I	II	III	
Average, %	Spectral	0.02	0.04	bulk	surface layer
\bar{C}^* , %	XSMA	Background	0.06 ± 0.05	0.15 ± 0.05	0.19 ± 0.05
C_{loc}^{**} , %	The same	The same	1.00	2.00	3.60

* The value \bar{C} shows the aluminum content averaged over all measurement points (50 – 60 points). At some points, the local concentration of Al differed sharply from the mean value. This value is designated by C_{loc} .

** Maximum values.

cording to the data from [1], basic oxides strengthen crystallization of quartz glass, crystallization is of a flaky nature, and the samples after crystallization have low mechanical strength. This can explain the appearance of defects in the form of flaky scaling on stirring rods made of quartz ceramics molded from "pure" slip at service temperature of 1450°C and above.

As opposed to calcium which causes rupture of Si – O – Si bonds in quartz glass, an increase in the mobility of glass lattice, and the possibility of its transformation, aluminum together with basic oxides form a quartz-like structure without ruptures, which decreases the thermal deformation and crystallization of quartz glass [1].

Since the appearance of calcium in the surface layer of ceramics is inevitable with the use of gypsum molds, in order to neutralize its negative effect, it is necessary simultaneously to introduce aluminum oxide into the slip, which happens in practice when slip is prepared in a porcelain mill with uralite balls. If the service temperature of a product does not exceed 1450°C, any of the mills and balls described above can be used to prepare slip.

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